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FINAL REPORT

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

DEVELOPMENT OF A PROTOTYPE EXPERIMENT

FOR TREATING CELSS AND PCELSS WASTES

TO PRODUCE NUTRIENTS FOR PLANT GROWTH

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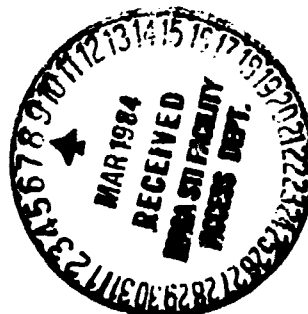Natick, Massachusetts 01760

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1.0   INTRODUCTION

Future long term spaceflights will require extensive recycling of
wastes to minimize the need for resupplying the vessel. The recycling
will occur in a fully or partially closed environment life support system
(CELSS or PCELSS). The National Aeronautics and Space Administration
(NASA) is interested in converting wastewater into potable water or water
for hydroponic farming as part of a CELSS. The development of technologies
for wastewater treatment that produce a minimum of by-products is essential
to meeting NASA's goal.

One process that can achieve good conversion of moderately
concentrated organic wastes in water (1-20% by weight) completely to carbon
dioxide and water is oxidation in supercritical water (Modell, 1982). Both
air (or oxygen) and many organics are completely miscible with
supercritical water, so there are no interphase mass-transport resistances
that can limit the overall oxidation reaction. The temperature of
supercritical water, which must be above $374^{o}C$, is also sufficient to have
rapid reaction kinetics for the oxidations. These are two reasons why
supecritical water is an excellent medium for oxidation of wastewater.

This Grant was used to conduct laboratory experiments to investigate
the treatment of CELSS or PCELSS. The supercritical water oxidation
process was the principal technology investigated, as it could produce
excellent destruction of wastes and had not been investigated previously.
This report summarizes the important results of the research and indicates
where detaled information from the research can be found. The original
proposal for the Grant included the tasks of:

1) Developing a waste model for a CELSS;

2) Collecting a representative waste for laboratory experiments;

3) Developing analytical methods to determine the fate of both
   organic and inorganic material during the labroatory treatment of
   the model or other wastes;

4) Treating the model waste or other material in a lab-scale
   oxidation apparatus;

and 5) Considering methods to remove salts from the product water that
may be harmfull to plant life in a CELSS.

2.0 ACCOMPLISHMENTS

2.1 Waste Model

The develpment of the waste model is explained in the Progress
Report for the period July 1, 1979 to December 31, 1980 for this Grant;
this Progress Report will hereafter be referred to as Modell(1980). This
report contains a review of food procesing waste technology and concluded
that the food processing waste model must be assembled from laboratory and
industrial food processing wastes and could not be made from synthetic
compounds. The compostion of a CELSS (with no animals) food processing
waste was calculated and presented. The total waste stream would also
include human metabolic wastes.

2.2 Representative Waste

The Georgia Institute of Technology entered a cooperative agreement with the Human Nutritional Research Lab of the U.S. Department of Agriculture to obtain freeze-dried samples of urine and feces as part of this Grant. Approximnately 2500 g of freeze-dried feces and 2300 g of freeze-dried urine were collected from four volunteers on a rigidly controlled and characterized diet. The diets of the volunteers and analysis of the urine and feces were reported (Modell, 1980).

2.3 Analytical Methods

The selection of the analytical methods for examing treated and raw CELSS wastes was conducted at the Georgia Institute of Technology. Gas chromatography instrumentation and methodology were developed to determine the composition of the gaseous effluents from the lab experiments. Inductively coupled plasma emission spectroscopy was selected and obtained is the best method to monitor the presence of inorganics in the liquid effluent from the lab experiments. Justification of these selections was reported earlier (Modell, 1980).

2.4 Waste Oxidation

Oxidation of the well-characterized urine and feces was conducted at both the Massachusetts Institute of Technology and MODAR, Inc. Price(1981) at MIT developed a continuous flow system for oxidizing a slurry of urine and feces under subcritical (wet oxidation) and supercritical conditions.

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Urine and feces were selected as major components of CELSS wastewater. A schematic of the apparatus is shown in Figure 1. Water, urine and feces were mixed, pressurized, and injected prior to mixing with compressed oxygen near the reactor inlet. The laminar-flow reactor was constructed of Hastalloy for strength and corrosion resistance. The effluent was cooled and separated into a gas and liquid fraction at atmospheric pressure, which were then analyzed for chemical composition. A similar flowsheet, and much of the same equipment, was used by Timberlake and coworkers (1982).

A feed of 650-1800 ppm TOC from urine and feces was oxidized at flows up to 0.42 cm^3/s with stoichiometric or excess oxygen (Price, 1981). The reactor was operated between 277 to 443°C, and 15.7 to 27.9 MPa. Between 88 and 93% of the TOC was eliminated in four minutes at 400°C, although the depressurized gas contained up to 10% carbon monoxide. The conversion of COD was 53% at wet oxidation conditions of 292°C and 15.7 MPa for 23 minutes. Weitzman(1977) achieved a conversion of 88% under similar nominal conditions but with a different feed composition, oxygen flowrate and an agitated reactor. Price's work demonstrated the ability to rapidly oxidize urine and feces in supercitical water, but that different operating conditions were needed to complete the conversion of organics to carbon dioxide.

Timberlake et al.(1982) at MODAR, Inc. continued investigating the applicability of the supercritical water oxidation process to CELSS by oxidizing urea in supercritical water. The reactor residece time was less than one minute at a liquid flow of 25 cm^3(NTP)/min, the exit temperature was greater than 550°C, and the pressure was greater than 21.5 MPa.

Solutions containing 10% urea were oxidized at average reactor wall temperatures between 561 and 670°C. Urea was 99.9% converted to nitrogen
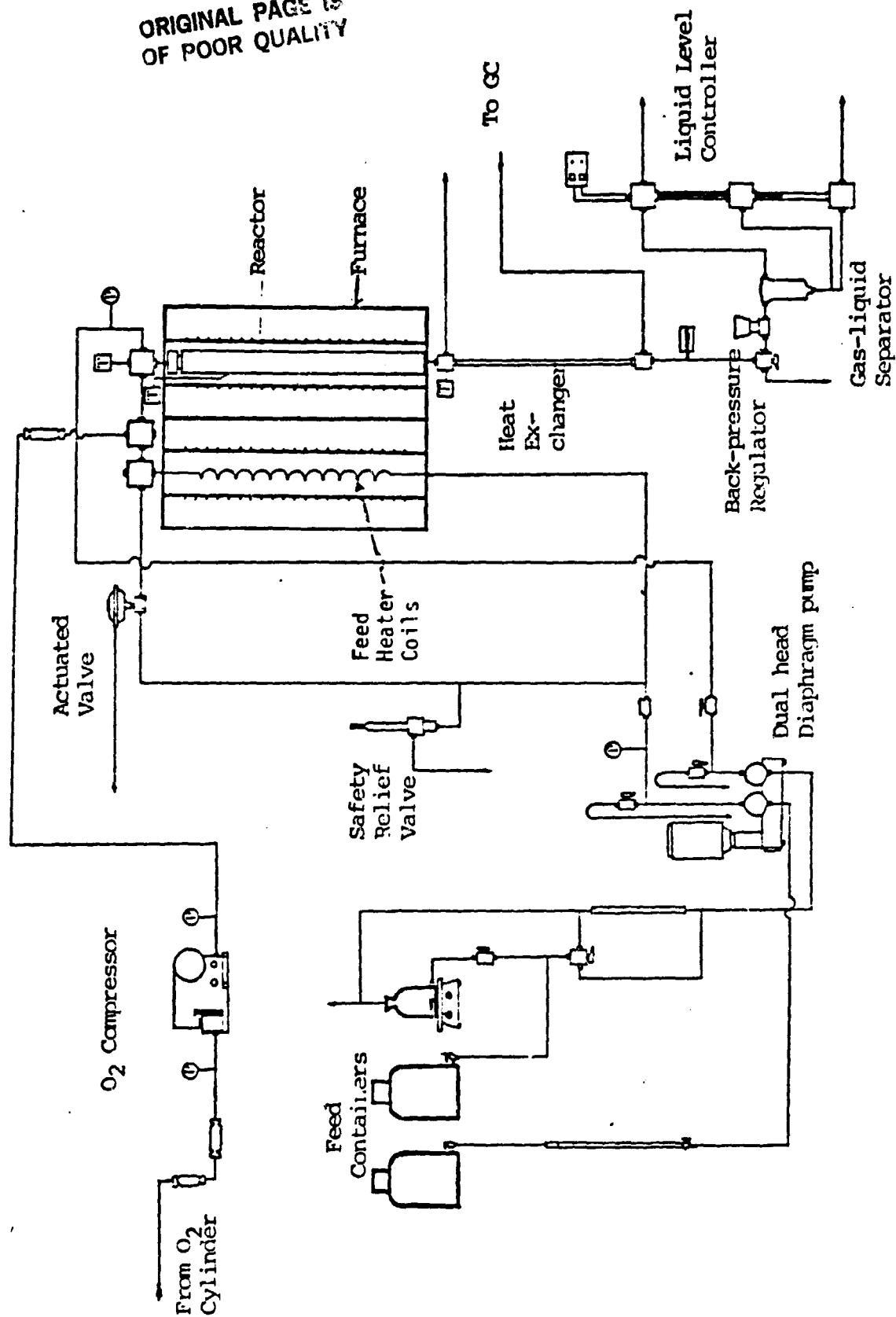
Figure 1 . Continuous Flow System for Oxidation in Supercritical Water(Price, 1981)

and carbon dioxide at 670°C. Nitrogen mass balances at other temperatures did not close greater than 74%, probably due to unquantified nitrogen in residual solids and gas phase ammonia, although no toxic NO_x were detected in the gas. The depressurized liquid contained 26% of the initial nitrogen as ammonia below 600°C, and about 5% at 621 and 632°C. Ammonia was the principal impurity in the effluent, and appears to be only slowly oxidized.

The mechanism for urea oxidation was postulated as hydrolysis of urea to ammonia and carbon dioxide, followed by free-radical oxidation of ammonia to nitrogen (Timberlake, et al., 1982). A greater availability of free radicals (such as hydroxyl radicals) could increase the reaction rate at lower temperatures. These radicals could occur if urea is oxidized with other, organic, components as in real wastewater.

The oxidation of ammonia as a function of reactor temperature was further investigated at MODAR, Inc. to help define the minimum temperature at which extensive oxidation of ammonia occurs. Experiments that were not reported previously (Timberlake et al., 1982) are described here. Mixtures of 4.4-4.8% by weight urea in water were oxidized with 36-67% excess oxygen, at a normal liquid flow of about 21 cm³/min, and at an average external wall temperature between 640 and 710°C. The exact conditions are listed in Table 1, which shows the incremental changes in reactor temperature, the addition of methyl ethyl ketone (MEK) in Run 232 as a solvent fuel, and the absence of an oxidant in Run 233, a reforming run. Other operating conditions were constant in all the runs.

The analytical results from these experiments were used to calculate the distribution of carbon and nitrogen between the liquid and gas phase effluents, the percentage recovery for carbon and nitrogen and the

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Table 1

Runs 227-230, 232, 233 Run Conditions

	227A	227B	228A	228B	229	230	232	233 (sample 9)
Feed Composition	20 wt% urea	20 wt% urea	20 wt% urea	20 wt% urea	20 wt% urea	20 wt% urea	18 wt% urea + 9 wt% MEK	20 wt% urea
Feed Density	1.053	1.053	1.053	1.053	1.053	1.053, 0.805	1.053	1.055
Oxidant Composition	38.7 mol% O₂ in He	38.7 mol% O₂ in He	37.5 mol% O₂ in He	37.5 mol% O₂ in He	37.7 mol% O₂ in He	37.7 mol% O₂ in He	37.7 mol% O₂ in He	He
Steady State Samples	12:30-14:29, 3-6	16:00-18:29, 10-14	11:30-13:29, 7-10	16:00-18:29, 16-20	10:00-11:59, 4-7	13:00-14:59, 2-5	15:00-15:59, 3-4	16:30, 9
Flow Rates: sccm								
Water	15.5	16.2	15.5	15.7	15.4	15.6	18.1	17.2
Feed	5.2	5.3	5.2	5.3	5.2	5.3	5.5, 0.7	5.1
Coolant H₂O	1.0	1.1	1.0	1.1	1.0	1.0	0.9	0.9
Gas Effluent	2369	2434	2217	2633	2515	2655	3790	1391
Liquid Effluent	22.4	24.0	22.1	20.8	21.6	22.6	24.5	24.5
Reactor Inlet Composition (Gas-Free Basis)								
wt% urea	4.8	4.7	4.8	4.8	4.8	4.8	4.6	4.4
wt% MEK	—	—	—	—	—	—	2.2	—
Stoichiometric O₂-excess	67%	50%	41%	36%	59%	61%	20%	—
Average Reactor Wall T (°C)	640	674	688	710	666	694	549	700 (sample 9)

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percentage conversion of ammonia to molecular nitrogen. The calculated quantities are listed in Table 2.

The most significant result of these experiments is the demonstrated correlation between reactor temperature and conversion of ammonia to molecular nitrogen, as shown in Figure 2. The temperatures plotted are averages of thermocouple readings taken at various locations along the outside wall of the reactor. They are probably not good estimates of the internal reactor temperatures and should be used as relative rather than absolute values. Nevertheless the correlation supports the hypothesis from the work of Timberlake and coworkers (1982) that above some "kindling" temperature, ammonia oxidation to molecular nitrogen increases rapidly.

The results from Run 232 show little effect of adding a solvent fuel on the oxidation of ammonia, although the reactor temperature for this run, despite the added fuel, was lower than necessary to achieve the desired oxidation. The reforming run (233) was conducted to determine if cyanide is formed during the thermal decomposition of urea in the absense of an oxidant. Ammonia in the liquid phase accounted for 99.5% of the urea nitrogen. One sample at the highest temperature (700°C) had 0.31 ppm CN- nitrogen. This value is near the lower limit of detection for the analytical method, a titration, and may be noise or an indicator blank. It is unlikey that cyanide formation would occur under normal operationg conditions.

This work demonstrates that ammonia can be oxidized in supercritical water, and without the formation of cyanide. The presence of organic material with urea or ammonia in a waste stream may influence the exent and nature of the oxidative reactions. Future experiments should examine the interaction of urea and organics in oxidation in supercritical water.
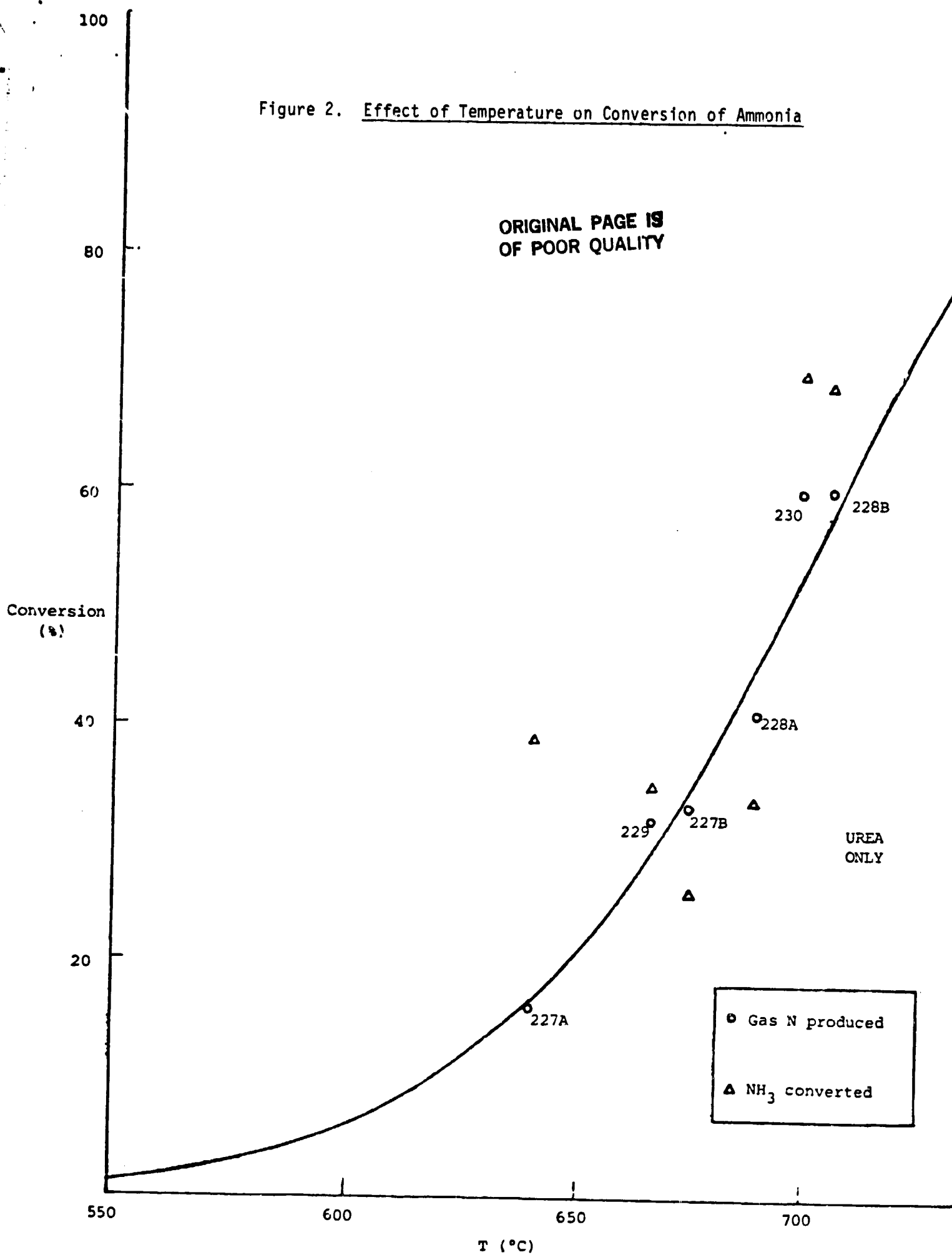
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Table 2

Runs 227-230, 232, 233 Results

Run	Carbon			Nitrogen			
	% in gas	% in liquid	% Recovery	% in gas	% in liquid	% Recovery	% Conversion to N_2
227A	0.2	109.0	109.2	15.5	61.4	76.9	15.6
227B	6.0	102.7	108.7	32.8	74.2	107.0	25.7
228A	9.1	66.7	75.8	41.1	63.5	104.7	34.5
228B	28.3	52.9	81.2	60.3	30.7	91.0	59.8
229	5.9	75.8	81.7	31.9	64.7	96.6	27.3
230	30.9	57.4	88.3	60.1	29.5	89.6	60.5
232	42.6	15.6	58.2	37.0	82.0	119.0	8.8
233	—	105.1	105.1	—	95.2	95.2	—

Figure 2. Effect of Temperature on Conversion of Ammonia

2.5 Salt Separation

The process of oxidation in supercritical water also offers a
conceptually simple method to remove salts from treated wastewater.
Inorganic salts are insoluble in supercritical water above about $500^{o}C$, due
to the low density and dielectric constant of water under these conditions
(Martynova, 1976; Marshall, 1976). Salts could be removed from treated
wastewater by a simple fluid-solids separator, such as by a cylcone
separator. This discovery eliminates the need for any low temperature and
pressure salt separation system in a CELSS. The performance of a cyclone
in the hot, high pressure environment of the supercritical water must be
tested in future research.

3.0 REFERENCES

3.1 Publications Supported by this Grant

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3.2 Other Publications

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